PATENT SPECIFICATION

683,128

Date of filing Complete Specification: June 26, 1950.

Application Date: July 22, 1949. No. 19291/49.

Complete Specification Published: Nov. 26, 1952.

Index at acceptance:—**Classes 2(iv)**, D2, F; **and 15(ii)**, B2b(1g:2c2).

COMPLETE SPECIFICATION

Improvements in and relating to Dyestuff Preparations, and the Dyeing of Cellulosic Materials such as Paper, therewith.

We, THE GEIGY COMPANY LIMITED, a British Company, of National Buildings, Parsonage, Manchester, in the County of Lancaster, and WILLIAM CARR, a British Subject, of 3, Berkeley Avenue, Victoria Park, Manchester, in the County of Lancaster, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to improvements in dyestuff preparations and in the process of dyeing cellulosic material, including non-woven cellulosic sheet material such as paper.

The dyeing of paper involves certain difficulties in producing colourations of sufficient strength, brightness and fastness to light. Since non-woven cellulosic sheet material, such as paper, has to be dyed in the pulp form the application of dyestuffs is often somewhat difficult.

It has been known for many years to make lakes from basic dyes and heteropoly acids. These are the so-called Fanal pigments and are made by reacting basic dyes with salts of heteropoly acids in aqueous media so that the lakes are precipitated and it has been proposed to carry out this reaction with the components in a damp or moist condition and in presence of a dispersing agent and an inert diluent, the product being afterwards dried.

According to one feature of the present invention there is provided a dyestuff preparation comprising a dry powdered mixture of a basic dye, a heteropoly acid known to be capable of forming a lake with a basic dye and a dispersing agent, preferably an anionic dispersing agent such as a sulphonate. Suitable dispersing agents are, for instance, sodium lignin sulphonate and the sodium salt of a condensation product of naththalene sulphonic acid and formaldehyde. With the acid of such dry, powdered dyestuff preparations, we are able to obtain level dyeings on cellulosic materials of good fastness to light by applying to the material the product obtained by dispersion of the dyestuff preparation in an aqueous medium such as water the resulting dispersion being very effective for the dyeing of cellulosic materials.

The feature which distinguishes the present invention from the prior proposals is that the basic dye, heteropoly acid and dispersing agent are mixed together in a dry, powdered form. The ingredients of this mixture are all soluble in water but when the mixture is mixed with water they immediately produce an insoluble product. It would not have been expected that the laking process would proceed so quickly and without heating. The dry mixtures of water-soluble ingredients give, when added to water or other aqueous media, very fine dispersions which are very stable and persist in most cases for several days. If they do settle out, the sediment is soft and bulky and readily re-disperses.

The preferred dispersing agent is "Belloid" T.D.

"Belloid" is a Registered Trade Mark and "Belloid" T.D. is a dispersing agent which is a sodium salt of a condensation product of naphthalene sulphonic acid and formaldehyde, which is readily obtainable. The invention is not limited to the use of this dispersing agent.

The preferred heteropoly acids employed in the present invention are those consisting of a phosphomolybdic acid, a phosphotungstic acid or a phospho-molybdotungstic acid or such an acid in which all or part of the phosphorus, molybdenum or tungsten is replaced by vanadium or selenium. These complex acids are well known and are used in the manufacture of pigments

[Price 2/8]

Price 4s 6d

from basic dyestuffs. They are generally formed by the acidification of mixed solutions of salts of the respective acids. In this specification and the appended claims the term "heteropoly acid" includes the so-called reduction products (see Specification No. 313,209).

According to another feature of the invention, there is provided a process for dyeing cellulosic materials by applying to them the product obtained by dispersing the dyestuff preparation defined above in an aqueous medium such as water. A preferred method of dispersing such dyestuff preparation is to form it into a paste with a small amount of cold water and then to add hot water, subsequently bringing the mixture to the boil.

The process of the invention is particularly applicable to the dyeing of non-woven cellulosic sheet material such as paper in the course of its manufacture.

According to a further feature of the present invention, therefore, the process of dyeing of cellulosic non-woven sheet material such as paper comprises adding to the pulp, before the addition of sizing agents, the product obtained by dispersing the dyestuff preparation defined above in an aqueous medium such as water.

According to yet another feature of the invention, the process of dyeing of cellulosic material such as paper or textiles comprises padding the material through the product obtained by dispersing the dyestuff preparation defined above together with a water-soluble binding or stiffening agent such as water-soluble gum or starch in an aqueous medium such as water, and subsequently drying the resulting padded material, for example, by passing it over a steam heated cylinder.

According to a still further feature of the invention the process of coating non-woven cellulosic materials such as paper comprises dispersing the dyestuff preparation defined above in an aqueous medium such as water, mixing the dispersion with suitable binders in the necessary proportions to give a correct coating consistency, applying the mixture to paper as a coating and then allowing the paper to dry.

By dyeing cellulosic materials with dyestuffs from such dyestuff preparations, the brightness and strength of the dyestuff are substantially unimpaired, whereas their light-fastness is considerably increased.

The dyestuff preparation may contain more than one basic dye and more than one complex acid, but as will be seen it contains essentially three components—firstly, the dyestuff component, secondly, the complex acid component and thirdly, the dispersing agent component. All of these components are obtainable in the form of fine dry free-flowing powders so that the preparation can be made by simply dry mixing the powders to give a uniform mixture. If any of the components is in a lumpy form, dry grinding and mixing of the components is required to give a uniform free-flowing powder mixture.

The relative proportions of the components are not critical but it has been found that the best results are obtained if the components are present in approximately the following relative proportions, by weight:—

Dyestuff Components	*Complex Acid Component*
30 to 50 parts.	40 to 60 parts.

Dispersing Agent Component
Up to 20 parts.

The invention, however, is not limited to these proportions.

The following are Examples of some preferred dyestuff preparations according to the present invention, but the invention is not limited to these Examples.

EXAMPLE 1.

Yellow

Auramine O 150%	35	parts
Complex Acid	57.5	„
"Belloid" T.D.	7.5	„
	100	„

EXAMPLE 2.

Magenta

Rhodamine B. 500%	40	parts
Complex Acid	52.5	„
"Belloid" T.D.	7.5	„
	100	„

EXAMPLE 3.

Green

Auramine O 150%	17.5	parts
Malachite Green Pdr. ...	17.5	„
Complex Acid	57.5	„
"Belloid" T.D.	7.5	„
	100	„

EXAMPLE 4.

5 gms. of the yellow powder prepared as in Example 1 are dispersed in 100 mls. of water by forming the powder into a paste with a small quantity of water and adding the remaining water hot, then bringing the mixture to the boil. 6 to 10 gms. of a water-soluble starch are incorporated during preparation of the dispersion. Other aqueous binding or stiffening agents can, of course, be used.

Paper is then padded through this suspension and dried by passing over (say) steam heated cylinders. The resulting material is evenly coloured and possesses good fastness to light.

EXAMPLE 5.

4 gms. of the magenta powder, whose constitution is given in Example 2, are dispersed in 100 mls. of water as described in Example 4.

10 gms. of alum sulphate (10% solution) are precipitated at 70°C. with 4.8 gms. sodium carbonate in 10% solution.

The suspension of magenta powder described above is added and then 11 gms. of barium chloride (as a 10% solution) are added.

The lake is filtered off and washed twice at the pump and 2 parts by weight of the resultant pulp lake are mixed with 1 part of a suitable aqueous binder such as a 16% solution of casein. The mixture is then coated on paper and dried. The resulting coating is a bright magenta in shade, free from specks and will take a high degree of calendering.

EXAMPLE 6.

5 gms. of the green powder as prepared in Example 3 are dispersed in 100 mls. of water in the manner described in Example 4. 3mls. of this suspension are added to 10 gms. china clay and 3 mls. of water added. These are mixed together and enough of a 16% casein solution or other binder is stirred in to give a mixture of correct consistency for coating. The mixture is applied to paper as a coating and allowed to dry. The resulting coating is free from specks, of a bright shade, uniform in colour intensity and will take a high degree of calendering.

For use in dyeing paper, the dyestuff preparation such as any of those described in the foregoing Examples is dispersed in water and then added to the paper pulp in the beater before the addition of the customary sizing agents such as size and alum. The resultant dyeings are free from two sided effects and are bright and strong in shade, with excellent fastness to light. Their resistance to fading on exposure to light is much better than that of the corresponding basic dyes used in their manufacture.

They are suitable for use on better quality paper pulps, such as bleached sulphite, esparto and rag pulps whereas the basic dyes from which they are made are widely known in the paper trade to be unsuitable for use on these pulps owing to their poor affinity for them.

They can be fixed on to rag blotting pulp by the addition of 0.5% of aluminium sulphate without appreciably impairing its absorbency.

By the present invention a wide range of shades can be obtained on cellulosic material.

What we claim is:—

1. A new composition of matter comprising a dry powdered mixture of a basic dye, a heteropoly acid known to be capable of forming a lake with a basic dye and a dispersing agent.

2. A new composition of matter as claimed in Claim 1 in which the dispersing agent is an anionic dispersing agent.

3. A new composition of matter as claimed in Claim 1 in which the dispersing agent is the sodium salt of a condensation product of naphthalene sulphonic acid and formaldehyde.

4. A new composition of matter as claimed in any of Claims 1 to 3, in which the heteropoly acid is a phospho-molybdic acid, a phospho-tungstic acid or a phospho-molybdo-tungstic acid.

5. A new composition of matter as claimed in Claim 4 in which all or part of the phosphorus, molybdenum or tungsten is replaced by vanadium or selenium.

6. A dyebath comprising an aqueous dispersion of a composition as claimed in any of Claims 1 to 5.

7. A method of making an aqueous dyestuff dispersion which comprises mixing a dry powdered mixture, as claimed in any of Claims 1 to 5, to a paste with water, adding more hot water and subsequently bringing the mixture to the boil.

8. A method of making an aqueous dyestuff dispersion as claimed in Claim 7 which includes incorporating in the suspension a water-soluble binder or stiffening agent.

9. A method of making a coating composition which comprises dispersing in water a composition as claimed in any of Claims 1 to 5 and adsorbing the dispersion on to a carrier.

10. A coating composition as claimed in Claim 9 in which the carrier is china clay.

11. A process of dyeing cellulosic materials from a dyebath as claimed in Claim 6.

12. A process of dying non-woven cellulosic sheet materials during the course of their manufacture, in which an aqueous dispersion of a composition as claimed in any of Claims 1 to 5 is added to said materials during the course of said manufacture before the addition of any sizing agents.

13. A process of coating non-woven cellulosic materials such as paper which comprises applying to the surface thereof a coating composition made by the method claimed in Claim 9.

14. A process of padding cellulosic materials with an aqueous suspension of a composition as claimed in any of Claims 1 to 5 containing also a water-soluble binding or stiffening agent.

15. Cellulosic materials when coated, padded, or dyed by any of the processes claimed in the foregoing claims.

16. The new compositions of matter and methods of colouring cellulosic materials herein particularly described.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

Improvements in and relating to Dyestuff Preparations, and the Dyeing of Cellulosic Materials such as Paper, therwith.

We, THE GEIGY COMPANY LIMITED, a British Company, of National Buildings, Parsonage, Manchester, in the County of Lancaster, and WILLIAM CARR, a British Subject, of 3, Berkeley Avenue, Victoria Park, Manchester, in the County of Lancaster, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in dyestuff preparations and in the process of dyeing cellulosic material, including non-woven cellulosic sheet material such as paper.

The dyeing of paper involves certain difficulties in producing colourations of sufficient strength, brightness and fastness to light. Since non-woven cellulosic sheet material, such as paper, has to be dyed in the pulp form the application of dyestuffs is often somewhat difficult.

According to one feature of the present invention there is provided a dyestuff preparation comprising a dry powdered mixture of a basic dye, a complex inorganic acid and a dispersing agent, preferably an anionic dispersing agent such as a sulphonate. Suitable dispersing agents are, for instance sodium lignin sulphonate and the sodium salt of a condensation product of naphthalene sulphonic acid and formaldehyde. With the aid of such dry, powdered dyestuff preparations, we are able to obtain level dyeings on cellulosic materials of good fastness to light by applying to the material the product obtained by dispersion of the dyestuff preparation in an aqueous medium such as water.

It would appear that a reaction takes place between the components of the mixture when this is dispersed in water but whatever may be the mechanism of the reaction the resulting dispersion is very effective for the dyeing of cellulosic materials.

By complex inorganic acid we mean a phosphomolybdic acid, a phospho-tungstic acid or a phospho-molybdo-tungstic acid. These complex acids are well known and are used in the manufacture of pigments from basic dyestuffs. They are generally formed by the acidification of mixed solutions of salts of phosphoric acid, molybdic acid and tungstic acid. The different complex acids are characterised by the ratio of phosphorus to molyhdenum, phosphorus to tungsten or phosphorus to molybdenum and tungsten.

According to a further feature of the invention, there is provided a process for dyeing cellulosic materials by applying to them the product obtained by dispersing the dyestuff preparation defined above in an aqueous medium such as water.

The process of the invention is particularly applicable to the dyeing of non-woven cellulosic sheet material such as paper in the course of its manufacture.

According to a still further feature of the present invention, therefore the process of dyeing of cellulosic non-woven sheet material such as paper comprises adding to the pulp, before the addition of sizing agents, the product obtained by dispersing the dyestuff preparation defined above in an aqueous medium such as water.

By dyeing cellulosic materials with dyestuffs from such dyestuff preparations, the brightness and strength of the dyestuff are substantially unimpaired, whereas their light-fastness is considerably increased.

The dyestuff preparation may contain more than one basic dye and more than one complex acid, but as will be seen it contains essentially three components—firstly, the dyestuff component, secondly, the complex acid component and thirdly, the dispersing agent component. All of these components are obtainable in the form of fine dry free-flowing powders so that the preparation can be made by simply dry mixing the powders to give a uniform mixture. If any of the components is in a lumpy form, dry grinding and mixing of the components is required to give a uniform free-flowing powder mixture.

The dyestuff preparations of the present invention are not soluble in water, although all the ingredients from which they are made are water-soluble. On being added to water or other aqueous media, they give very fine dispersions which are very stable and persist in most cases for several days. If they do settle out, the sediment is soft and bulky and readily re-disperses.

The relative proportions of the components are not critical but it has been found that the best results are obtained if the

components are present in approximately the following relative proportions, by weight:—

Dyestuff Components	*Complex Acid Component*
30 to 50 parts.	40 to 60 parts.

Dispersing Agent Component
Up to 20 parts.

The following are Examples of some preferred dyestuff preparations according to the present invention:—

EXAMPLE 1.

Yellow

Auramine O 150%	35	parts
Complex Acid	57.5	„
" Belloid " T.D.	7.5	„
	100	„

EXAMPLE 2.

Magenta

Rhodamine B. 500%	40	parts
Complex Acid	52.5	„
" Belloid " T.D.	7.5	„
	100	„

EXAMPLE 3.

Green

Auramine O 150%	17.5	parts
Malachite Green Pdr. ...	17.5	„
Complex Acid	57.5	„
" Belloid " T.D.	7.5	„
	100	„

" Belloid " is a Registered Trade Mark and " Belloid " T.D. is a dispersing agent which is a sodium salt of a condensation product of naphthalene sulphonic acid and formaldehyde, which is readily obtainable. The invention is not limited to the use of this dispersing agent.

For use in dyeing paper, the dyestuff preparation such as any of those described in the foregoing Examples is dispersed in water and then added to the paper pulp in the beater before the addition of the customary sizing agents such as size and alum. The resultant dyeings are free from two sided effects and are bright and strong in shade, with excellent fastness to light. Their resistance to fading on exposure to light is much better than that of the corresponding basic dyes used in their manufacture.

They are suitable for use on better quality paper pulps, such as bleached sulphite, esparto and rag pulps whereas the basic dyes from which they are made are widely known in the paper trade to be unsuitable for use on these pulps owing to their poor affinity for them.

They can be fixed on to rag blotting pulp by the addition of 0.5% of aluminium sulphate without appreciably impairing its absorbency.

By the present invention a wide range of shades can be obtained on cellulosic material.

Dated this 21st day of July, 1949.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4. 39/244.—1952.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.